Chemical shift anisotropies in silicon containing three-membered rings. An ab initio study

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Received 21 March 1995; in final form 15 May 1995

Abstract

Ab initio NMR shielding calculations were carried out for cyclic compounds containing the cyclotrisilane, silaoxirane, disilacyclopropane, silacyclopropane, cyclotetrasilane, cyclopentasilane and cyclohexasilane skeletons. Calculations were performed for all permethylated compounds, as well as for the fully tert-butyl substituted cyclotrisilane. Geometries were optimized at the SCF/3-21G(*) level while NMR shieldings were evaluated using large basis sets. The results reproduce the high ^{29}Si chemical shift anisotropies observed in three-membered rings. Calculations on strongly distorted models with local geometries similar to those in small rings suggest that the high anisotropy is due to the distorted geometry around the Si atom, not to special bonding effects in the three-membered rings.

1. Introduction

Measurements of the chemical shift anisotropies have proved useful in probing the electronic structure of several compounds [1]. In recent solid state NMR experiments high chemical shift anisotropies (CSA) were observed for the ^{29}Si in two cyclotrisilanes and in a siloxirane [2]. The spread in the ^{29}Si shielding tensor components was found to be around 200 ppm in these compounds. This is markedly higher than the values measured for cyclopropane (≈ 60 ppm) [3] and for a larger silicon containing ring (≈ 60 ppm in $(Ph_2Si)_4$) [4]. Although these are

high anisotropies and Cavalieri et al. [2] consider them unusual, it may be noted that relative to the usual spread of ^{29}Si shieldings (about 600 ppm, see Ref. [5]), the observed anisotropy in the three-membered silicon rings is not larger than the ^{13}C anisotropy in cyclopropane relative to the range of carbon shieldings (≈ 200 ppm). Recent developments in computational chemistry [6–8] allow the reliable calculation of NMR shieldings of molecules close in size to the actual compounds studied by Zilm and co-workers. The purpose of this study was to determine if the high CSAs of these systems is reproduced by ab initio calculations, and whether they indicate an exceptional electronic structure. The calculation of anisotropies is simpler than that of absolute shieldings since they are relative values, and it is also more instructive, as their experimental determination is more difficult.

[1] Part of a Diploma Thesis submitted to the Eötvös University, Budapest, Hungary.

2. Calculations

Hexamesityl-cyclotrisilane (1), hexa-tert-butyl-cyclotrisilane (2) and tetramesityl-siloxirane (3) were studied in the experiments of Cavalieri et al. [2]. However, hexamethyl-cyclotrisilane (4) and tetramethyl-siloxirane (5) were chosen as model systems (see Fig. 1). These can be calculated at a reasonable computational cost even with the large basis sets [9] required for the accurate calculation of chemical shifts. Thus the effect of the large substituents, which can distort the original D_{3h} symmetry of the ring [10,11], is also eliminated. Nevertheless, calculations for 2 were also possible allowing direct comparison between theory and experiment. Geometries were optimized using 3-21G(*) basis sets [12] and the TX90 package [6]. The only exception was 2, which was optimized by TURBOMOLE [13]. The structural parameters are shown in Table 1. Since these compounds (with the exception of 2) have not been synthetized, the calculated structures cannot be directly compared with experiment. The optimized structures of 4 and 5 are close to the known structures of other similar three-membered rings. The differences can be ascribed mainly to the bulky protective substituents (mesityl, tert-butyl, neopentyl) in the experimentally available compounds. The calculated structure of 2 agrees well with experiment.

Table 1
Calculated and measured structural parameters for several silicon-containing three-membered rings

Parameter [a]	2 calculated	2 experimental [b]	Experimental [c]	4 calculated
r(Si–Si)	247.5	251.1	239.1	233.6
r(Si–C)	198.1	197.0	191.2	189.6
angles				
C–Si–C	105.8	105.7	119.3	112.1
Si–Si–C	121.5 [d]	121.5 [d]	116.0	118.9

Parameter	5 calculated	3 experimental [e]		
r(Si–Si)	219.6	222.7		
r(Si–C)	187.4	187.8		
r(Si–O)	168.8	173.3		
angles				
Si–Si–O	49.4	50.0		
Si–O–Si	81.2	80.0		

[a] Bond lengths in pm, angles in degrees. 2 = hexa-t-butyl-cyclotrisilane; 4 = hexamethyl-cyclotrisilane, 5 = tetramethy-siloxirane, 3 = tetramesityl-siloxirane.
[b] See Ref. [7].
[c] Hexa-neopentyl-cyclotrisilane, average of two conformers in the solid phase: Ref. [14].
[d] Average value, according to the D_3 symmetry the C–Si–C plane is not perpendicular to the plane of the ring (the calculated deviation is 1.6°).
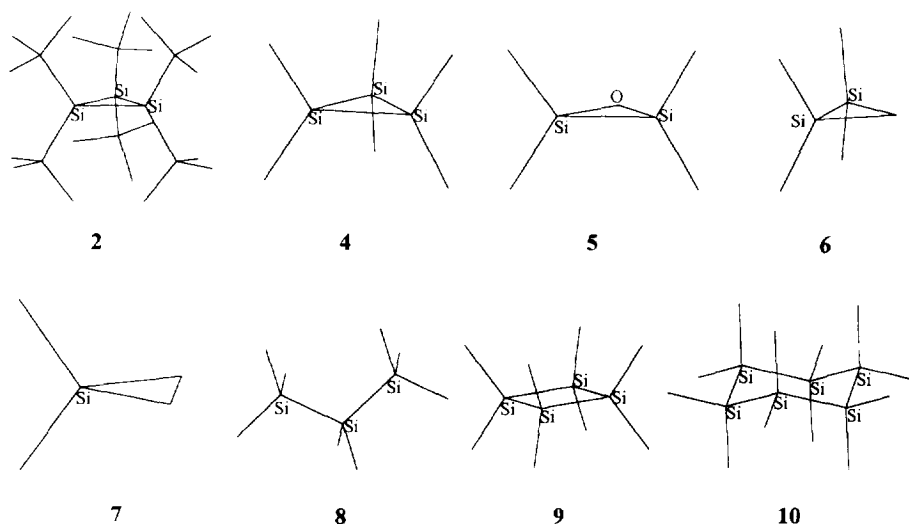[e] Ref. [15].

Fig. 1. Schematic structures of molecules 2 and 4–10.

Nuclear shieldings were evaluated by the GIAO method using the TX90 program [6]. NMR calculations were performed using the triple zeta basis of Schäfer et al. [16] augmented on Si with two additional d-type polarization functions, which are needed for the good description of Si shieldings [6] [12s/7s (5121111) 9p/5p (51111) + 3d]. The new exponents were obtained by dividing the last exponent by 3. In the case of 2 the use of a locally dense basis [17] was necessary to diminish the computational cost. We retained the large TZ3P basis on the silicon atoms but used only a DZ basis [16] on the quaternary carbons, and MINI basis [18] on the other atoms.

3. Results and discussion

Table 2 compares the calculated and experimental values of the principal components of the shielding tensor, their average, spread and anisotropy for the compounds measured in Ref. [2], 1, 2 and 3, with those calculated for 2, 4 and 5. The calculations reproduce the high values of the ^{29}Si CSA, about 200 ppm. The calculated spreads and anisotropies are somewhat larger than the observed ones. This appears to be a general phenomenon in SCF calculations [7,8] and may be due to the neglect of electron correlation, and vibrational averaging. The calculations also provided the orientations of the principal axes of the tensor. The high CSA is due to the component perpendicular to the plane of the ring (σ_{33}) both in 4 and 5, since this direction is more shielded by nearly 200 ppm than the other two. In 4 the smallest component is along the bisector of the

Table 2
Principal components of the shielding tensor (σ), their spread ($\sigma_{33} - \sigma_{11}$), the CSA [$\Delta\sigma = (\sigma_{11} + \sigma_{22})/2 - \sigma_{33}$] and the isotropic average for cyclotrisilanes and siloxiranes in ppm

Molecule	σ_{11}	σ_{22}	σ_{33}	Isotropic	Spread	$\Delta\sigma$
1 exp. [b,c]	333.5	415.5	523.5	424.1	190	149
	318.5	410.5	535.5	422.9	217	171
2 exp. [b]	278.5	375.5	465.5	372.9	187	138.5
2 calc. [a]	273.7	401.7	510.3	395.2	237.57	173.04
4 calc. [a]	372.9	404.4	574.7	450.6	201.86	186.10
3 exp. [b]	307.5	388.5	490.5	396.2	183	142.5
5 calc. [a]	293.1	369.8	504.6	389.2	211.58	173.22

[a] The shift reference in the experiments was TMS, the absolute shielding of which is 368.5 ± 10 ppm [23].
[b] See Ref. [2].
[c] Two silicon signals were observed probably due to the distortion of the ring.

Si–Si–Si angle, in 5 it is close to the Si–Si line. Fig. 2 depicts the approximate orientation of the principal axes. Their orientation in 2 is nearly the same as in 4 except for a slight rotation (1.6°) around σ_{33}.

There is only a modest number of experimentally determined Si-29 shielding tensors [4]. To aid in the interpretation of the high anisotropy, calculations on a series of compounds related to the cyclotrisilane 4 were also carried out, using the same method (3-21G($*$) basis for geometry optimization, TZ3P basis [16] for shielding calculation). The molecules chosen were 1,1,2,2-tetramethyl-1,2-disilacyclopropane (6), 1,1-dimethyl-silacyclopropane (7), octamethyl-trisilapropane (8), octamethyl-cyclotetrasilane (9) and dodecamethyl-cyclohexasilane (10) (see Fig. 1). The
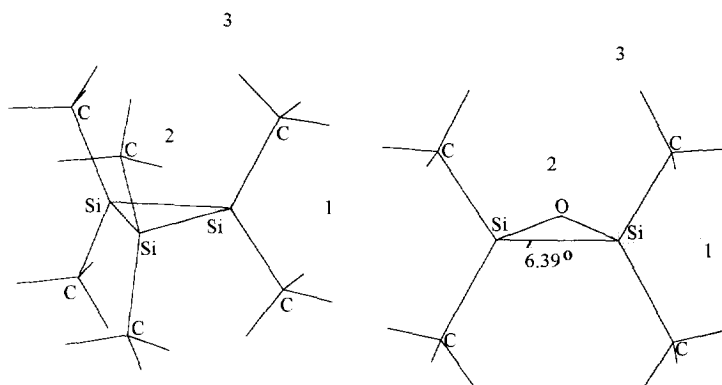

Fig. 2. The orientation of the principal axes of the shielding tensor in 4 and 5.

Table 3
Calculated shielding tensors in molecules **6–10**

Molecule	Si–Si–X (deg)	σ_{11} [a] (ppm)	σ_{22} [a] (ppm)	σ_{33} [a] (ppm)	Isotropic (ppm)	$\Delta\sigma$ (ppm)
6	54.0	339.9 *	379.7 *	571.9	430.5	212.1
7	51.7	352.4	359.2	629.1	446.9	273.2
8 [b]	112.8	432.6	404.0	452.6	429.7	34.2
9	88.1	402.6 *	402.1	433.4 *	412.7	31.0
10	111.9	424.8	404.2	445.8 *	424.9	31.1

[a] The notation used here differs from the usual convention, see text. Asterisks denote principal values which are not exactly analogous in the series due to the lack of local symmetry.
[b] Shielding of the central Si atom.

calculations of the shieldings of **10** had to be carried out using a locally dense basis (Schäfer et al. [16] TZ3P on Si, DZP on C, DZ on H). Experimental geometries and shieldings are not yet available for these molecules. The results of these calculations are summarized in Table 3. In order to facilitate comparisons we retained the order of the principal values in **4**, i.e. σ_1 falls on the bisector of the Si–Si–Si angle and σ_{33} is perpendicular to the plane of the ring. In some cases (marked by an asterisk in Table 3) this correspondence is not perfect because of distortions in the local symmetry.

In the series **6–10** only the three-membered rings have high ^{29}Si anisotropies, due to the strongly shielded σ_{33} component. In **4**, **6**, **7** and **8**, where σ_3 can be directly compared, $\Delta\sigma$ increases as the Si–Si–X angle decreases. Cremer and Gauss had also studied similar three-membered rings having 1, 2 and 3 silicon atoms in the ring [19]. They found that the strain energies were primarily determined by the bond angles at the Si atoms.

It is to be expected that the shielding component perpendicular to a symmetry plane is determined by the geometry (mainly the angle) in the plane. Thus the high shielding of σ_{33} is the consequence of the small angle forced on the Si atom by the ring. However, it is difficult to separate the effects of the geometry from the effects of the bonding, and this has caused considerable argument [20] in the discussion of the strain energy.

We attempted to separate the two effects by using the following model system. One of the C–Si–C angles (α) in tetramethylsilane was constrained to several values between 60 and 116 degrees. The
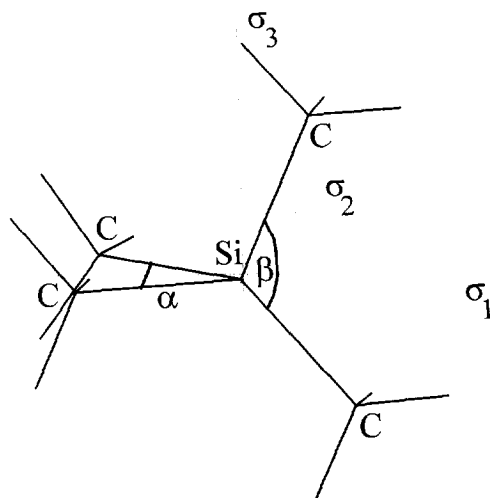

Fig. 3. The notation used for the distorted TMS molecules.

other geometry parameters were optimized at the SCF/3-21G * level, and the Si shieldings were calculated using the large TZ3P basis [16]. The geometry and the direction of principal axes is shown in Fig. 3; Table 4 lists the results. Although some of the constrained geometries are very high in energy, the bonding type is essentially the same as in equilibrium. In particular no new bonds form between the end groups. Even at the most severe deformation (CSiS angle 60°), the nonbonded C–C and the H–H distances are quite long (215 and 176 pm, respectively).

The results show that the anisotropy (CSA) increases dramatically as the angle becomes more acute, and the component perpendicular to the plane

Table 4
Calculated ^{29}Si shielding tensors in TMS molecules distorted to different extent. The anisotropy is defined here as $\sigma_{33} - (\sigma_{11} + \sigma_{22})/2$

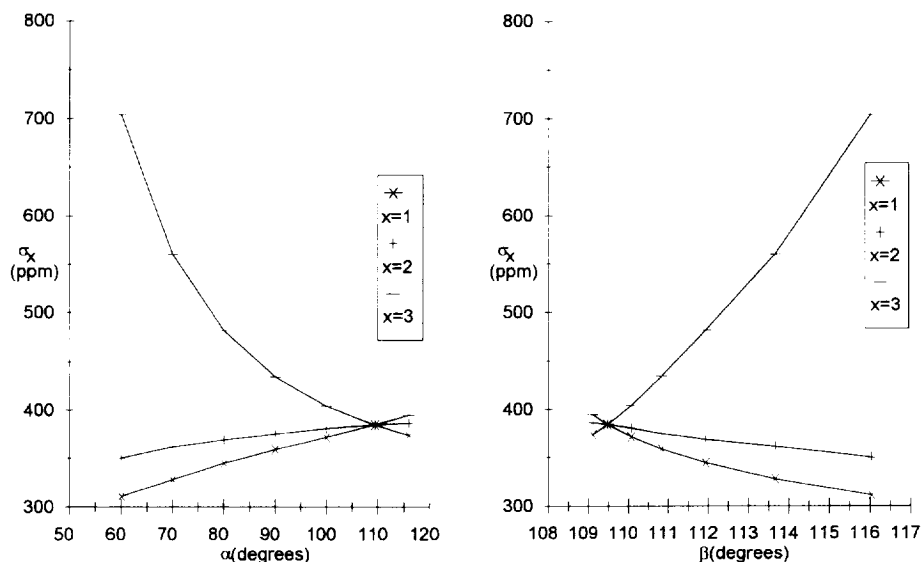| α (deg)	β (deg)	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	$\Delta\sigma$ (ppm)
60	116.04	311.31	350.13	704.84	374.12
70	113.66	328.07	361.62	560.9	216.06
80	111.93	344.91	368.71	482.21	125.39
90	110.83	358.97	374.97	434.78	67.82
100	110.07	371.66	380.61	404.76	28.62
109.47	109.47	384.75	384.75	384.75	0
116.03	109.11	373.65	386.46	395.12	– 15.06

Fig. 4. The principal elements of the shielding tensor in the distorted TMS molecules as a function of α and β.

of the constrained angle is primarily responsible for this, like in the cyclic compounds. The dependence of the principal shieldings on the two angles (α and β) is shown in Fig. 4. Both σ_{33} and the anisotropy correlates linearly with the angle β, opposite to the constrained angle. Assuming that the anisotropy is determined by the immediate environment of the nucleus, it would be more correct to use bent bond [21] angles instead of geometrical angles. Cremer and Gauss have calculated bent bond angles for three of the molecules studied here [6] (4, 6, 8). The anisotropy changes linearly with the equivalent of α as expected.

To study whether these result depend on the substituents, we have performed similar calculations on SiH_4. In this case no hyperconjugation effects can arise [22]. The shielding in the equilibrium geometry is isotropic, 478.0 ppm. If a H–Si–H angle is distorted to 60°, the pricipal values of the shielding tensor become 419.5, 454.4, 755.5 ppm in the order used in Fig. 2. This is very similar to the case of TMS, showing that the anisotropy is mainly determined by the asymmetry of the bond angles on silicon and not by the bonding partner.

Can this model explain the observed values in the four-membered ring and in carbon compounds? Direct comparison with model is difficult in oc-

tamethyl-cyclotetrasilane (9) because the ring is not planar and σ_{33} has an angle of 33.1° with the normal of the Si–Si–Si plane. The small calculated anisotropy (31 ppm, see Table 2) agrees qualitatively with the prediction of the model in Table 4 for an angle close to 90°.

Carbon NMR shieldings show a trend similar to Si but the anisotropy increases less dramatically with the angle distortion. This is shown by calculations on methane, analogous with those on SiH_4. At equilibrium the calculated ^{13}C shielding in methane is isotropic, 201.0 ppm. Distorting an angle to 60 degrees increases σ_3 to 273.6 ppm and the anisotropy to 76.3 ppm. This can be compared with the measured principal values of the shift tensor in cyclopropane, 22, 2, -36 ppm, respectively [3] (referenced to TMS). The shielding component perpendicular to the plane of the ring increases (the shift decreases) due to the angle distortion but the change is less than for silicon, in line with the smaller range of chemical shifts for carbon.

4. Summary

Silicon-29 NMR shieldings have been calculated by the ab initio gauge-including atomic orbital

(GIAO) SCF method for silicon-containing three-, four-, five-and six-membered rings, and for strained silicon and carbon model compounds. The calculation reproduce the observed strong anisotropy of the chemical shielding in three-membered rings, due to the increase in the principal shielding component perpendicular to the ring. Comparison with distorted open-chain molecular models show that the increase is caused by the distortion of the bond angles around the ring atoms. No special ring bonding effects need to be postulated to explain the experimental results. Carbon compounds, e.g. cyclopropane also show this phenomenon but it is more pronounced in the silicon analogues.

Acknowledgements

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